The Hydration of Nitriles Catalyzed by the Combination of Palladium Nanoparticles and Copper Compounds

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New catalysts based on Pd nanoparticles for the hydration of nitriles to amides were investigated. Copper compounds containing oxygen acted as effective promoters in the catalytic system. The catalysts could be used to prepare aromatic and aliphatic amides from the corresponding nitriles. Chloride ions significantly inhibited the catalytic performance.

Soluble nanoparticles[1] (NP) composed of a few tens to a few hundred atoms have a number of active sites with high-specific surface areas in the bulk phase. The chemical properties of NPs have recently attracted attention for diverse catalytic usage.[2] NP catalysts exhibit not only high selectivity like homogeneous catalysts but also recyclability like heterogeneous catalysts. Therefore, they meet the needs of modern green sustainable chemistry.[3] While there have been many reports on NP catalysts for oxidation[4] and hydrogenation,[5] their application to hydration has been limited.[6]

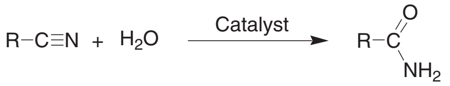
The catalytic hydration of nitriles is essentially an atom-economical reaction and an ideal sustainable method for the preparation of amides (Scheme 1).[7] Toshima and co-workers reported that NP comprising a palladium–copper alloy acts as a catalyst for the hydration of acrylonitrile.[6b–6d] We found that palladium and platinum single NPs acted as catalysts for the hydration of various nitriles without requiring the preparation of an NP alloy. In this paper, we report new catalysts composed of a single NP and a copper compound for selective production of amides.

The Pd and Pt NPs were prepared in the presence of a water-soluble polymer for the stabilization of NPs, poly(*N*-vinyl-2-pyrrolidone) (PVP), by reduction of the corresponding precursors, Pd^{II} acetate and $H_2Pt^{IV}Cl_6$, respectively.[8] The particle size of all NP samples were characterized by transmission electron microscopy. The average size of Pd and Pt NPs were 1.8 nm with the standard deviation (σ): 1.6×10^{-3} and 1.5 nm with $\sigma = 3.3 \times 10^{-4}$. Pd powder with 1000–1500 nm (Sigma-Aldrich Co.) was used as the comparative material for Pd NPs. All catalytic reactions were carried out using standard Schlenk techniques under argon. The products were detected by gas chromatography (Shimadzu Co., GC-2014) using nonpolar packed columns (Restek Co., Rtx-1 and Rtx-Wax).

We examined the hydration of benzonitrile using the NP-based catalysts, and the results are summarized in Table 1 with experimental conditions. The Pd-catalyzed reaction proceeded at 373 K in the presence of copper acetylacetonate [$Cu(acac)_2$] as a promoter to give benzamide in 87% yield (Entry 3). Catalytic activity was not observed for all NPs and Cu compounds (Entries 1 and 2). At 453 K, benzamide was obtained quantitatively (Entry 4). Some other copper compounds were also effective (Entries 5–7). When $Cu(NO_3)_2\cdot 3H_2O$ was used as a promoter, the product yield decreased (27%) (Entry 8). CuCl and $CuCl_2$ greatly inhibited the catalytic performance (Entries 9 and 10). On the basis of these results, it was suggested that a suitable promoter for the hydration would be a copper compound containing an oxygen atom. Iron and nickel compounds were ineffective as promoters in the reaction (Entries 11, 12, and 13). Cobalt(II) nitrate trihydrate, cobalt(II) diacetate 3-hydrate, and tin(II) chloride 2-hydrate were also ineffective (results not shown). In contrast to the Pd NP, the Pt NP catalysts showed low activities (Entries 14, 15, and 16). Pd powder (Entries 17 and 18) showed lower catalytic activity than the Pd NP. These results suggest that the active sites of Pd NPs, i.e., the vertex and edge atoms that are composed of coordinatively unsaturated atoms on the surface, behave effectively in the course of hydration. This is because Pd NPs have more atoms in proportion to the specific surface area than Pd powder.[9] Regarding Entries 9 and 10, there is a possibility that the dissociated chloride ion in the reaction media acted as an inhibitor in the reaction catalyzed by the NP system. Figure 1 shows the effects of NaCl as a chloride ion source on nitrile hydration using the NP catalyst. NaCl added at 0.01 and 0.02 mmol levels to Entry 3 significantly decreased the yield from 87% to 2.7% and 0.6%, respectively. These results provide further evidence that chloride ion has a negative effect on the hydration of benzonitrile. The same reasoning applies to the cases of Pt NPs, because the precursor material of Pt NPs includes chlorine. We think that Cl^- causes a decreased yield by inhibiting the coordination between Cu compounds with the NP surface, and/or the adsorption of substrate to the active site on the NP.

Table 2 shows the results of catalytic hydration of various nitriles. Our new catalysts were effective for various nitriles, e.g., aliphatic, aromatic, and heteroatom-containing aromatic nitriles. The hydration of less reactive aliphatic nitriles,[7c] e.g., butyronitrile and 3-phenylpropanenitrile, also proceeded. Nicotinamide, which is part of the vitamin B group, was prepared in 69% yield using $Cu(acac)_2$ as a promoter. An aromatic nitrile bearing an electron-donating group, *p*-methoxybenzonitrile, was also hydrated and the corresponding amide was obtained in 84% yield. The yield was comparable to that observed in the case of benzonitrile. In contrast to our results described above, Toshima's Pd–Cu alloy only gave acrylamide.

In summary, a new catalytic system (Pd NP–Cu compound) showed high catalytic activities for the hydration of various ni-



Scheme 1.

Table 1. The catalytic hydration of benzonitrile using the nanoparticle system[a]

Entry	Catalyst	Dia./nm	Promoter	Temp/K	Conversion/%[b]	Yield/%[b]
1	Pd NP	1.8	None	373	1	<1
2	None		$Cu(acac)_2$	373	<1	<1
3	Pd NP	1.8	$Cu(acac)_2$	373	91	87
4			$Cu(acac)_2$	453	>99	>99
5			$CuSO_4$	373	98	98
6			CuO	373	73	73
7			$CuCO_3 \cdot Cu(OH)_2$	373	96	96
8			$Cu(NO_3)_2 \cdot 3H_2O$	373	27	27
9			CuCl	373	<1	<1
10			$CuCl_2$	373	<1	<1
11			$NiSO_4$	373	<1	<1
12			$FeSO_4 \cdot 7H_2O$	373	<1	<1
13			$FePO_4 \cdot 4H_2O$	373	<1	<1
14	Pt NP	1.5	None	373	<1	<1
15			$Cu(acac)_2$	373	5	<1
16			$Cu(acac)_2$	453	37	7
17	Pd powder	1000–1500	$Cu(acac)_2$	373	<1	<1
18			$Cu(acac)_2$	453	62	59

[a]Reaction conditions: catalyst 0.01 mmol, promoter 0.02 mmol, benzamide 0.2 mmol, water 11 mmol, EtOH (solvent) 0.25 mL, 16 h. [b]GC analysis using internal standard technique.

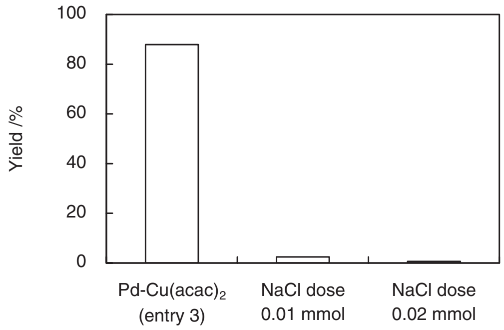
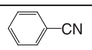
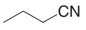
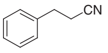
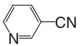
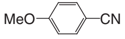


Figure 1. Effect of NaCl as Cl ion on the yield of benzamide (373 K).

Table 2. The catalytic hydration of various nitriles by the NP catalysts[a]

Nitrile	Yield/%		
	Promoter		
	None	$Cu(acac)_2$	CuO
	<1	88	73
	<1	36	30
	<1	90	75
	<1	69	62
	<1	84	25

[a]Pd NP 0.01 mmol, promoter 0.02 mmol, nitrile 0.2 mmol, water 11 mmol, 373 K, 16 h.

triles. More than 99% yield on benzonitrile hydration was recorded at 453 K by Pd NP–$Cu(acac)_2$. Chloride ion acted as an inhibitor in the catalytic hydration by the NP system. Further studies on the reactions and mechanism of NP catalysis are currently in progress.

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References and Notes

1 a) T. Teranishi, M. Miyake, *Chem. Mater.* **1998**, 10, 594. b) M.-C. Daniel, D. Astruc, *Chem. Rev.* **2004**, *104*, 293. c) B. He, Y. Ha, H. Liu, K. Wang, K. Liew, *J. Colloid Interface Sci.* **2007**, *308*, 105.

2 a) M. Haruta, T. Kobayashi, H. Sano, N. Yamada, *Chem. Lett.* **1987**, 405. b) Y. Shiraishi, N. Toshima, *Colloids Surf., A* **2000**, *169*, 59. c) K. Ebitani, K.-M. Choi, T. Mizugaki, K. Kaneda, *Langmuir* **2002**, *18*, 1849. d) M. Haruta, *Nature* **2005**, *437*, 1098. e) J. C. Serrano-Ruiz, A. López-Cudero, J. Solla-Gullón, A. Sepúlveda-Escribano, A. Aldaz, F. Reinoso, *J. Catal.* **2008**, *253*, 159.

3 a) D. Astruc, *Inorg. Chem.* **2007**, *46*, 1884. b) D. Astruc, in *Nanoparticles and Catalysis*, ed. by D. Astruc, Wiley-VCH, Weinheim, **2008**, Chap. 1, pp. 1–2.

4 a) K. Bergamaski, E. R. Gonzalez, F. C. Nart, *Electrochim. Acta* **2008**, *53*, 4396. b) L. M. Neal, H. E. Hagelin-Weaver, *J. Mol. Catal. A: Chem.* **2008**, *284*, 141.

5 a) X.-D. Mu, D. G. Evans, Y. Kou, *Catal. Lett.* **2004**, *97*, 151. b) G. Berhault, L. Bisson, C. Thomazeau, C. Verdon, D. Uzio, *Appl. Catal., A* **2007**, *327*, 32. c) J. M. Nadgeri, M. M. Telkar, C. V. Rode, *Catal. Commun.* **2008**, *9*, 441.

6 a) H. Hayashi, H. Nishi, Y. Watanabe, T. Okazaki, *J. Catal.* **1981**, *69*, 44. b) N. Toshima, Y. Wang, *Chem. Lett.* **1993**, 1611. c) N. Toshima, Y. Wang, *Langmuir* **1994**, *10*, 4574. d) Y. Wang, H. Liu, N. Toshima, *J. Phys. Chem.* **1996**, *100*, 19533.

7 Representative examples of catalytic nitrile hydration: a) S.-I. Murahashi, T. Naota, *Bull. Chem. Soc. Jpn.* **1996**, *69*, 1805. b) T. Ghaffar, A. W. Parkins, *J. Mol. Catal. A: Chem.* **2000**, *160*, 249. c) K. Yamaguchi, M. Matsushita, N. Mizuno, *Angew. Chem., Int. Ed.* **2004**, *43*, 1576. d) T. Oshiki, H. Yamashita, K. Sawada, M. Utsunomiya, K. Takahashi, K. Takai, *Organometallics* **2005**, *24*, 6287. e) A. Goto, K. Endo, S. Saito, *Angew. Chem., Int. Ed.* **2008**, *47*, 3607.

8 Y. Nakazaki, Jpn. Pat. Appl. 2005-264199.

9 J. R. Anderson, *Structure of Metallic Catalysts*, Academic Press, London, **1975**, p. 245.

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